

## Research Article

# Inhibition Effect of 1-Butyl-4-Methylpyridinium Tetrafluoroborate on the Corrosion of Copper in Phosphate Solutions

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The influence of the concentration of 1-Butyl-4-methylpyridinium tetrafluoroborate (4MBPBF<sub>4</sub>) as ionic liquid (IL) on the corrosion of copper in 0.5 M PO<sub>4</sub><sup>3-</sup> solutions of pH 2 and 4 was studied. The research involved electrochemical polarization method, and scanning electron microscopy (SEM) technique. The results obtained showed that the inhibition efficiency of corrosion of copper increases with an increase in the concentration of 4MBPBF<sub>4</sub> but decreases with increasing temperature. The thermodynamic functions of corrosion analysis and adsorptive behavior of 4MBPBF<sub>4</sub> were carried out. During the test, the adsorption of the inhibitor on the copper surface in the phosphate solutions was found to obey the Langmuir adsorption isotherm and had a physical mechanism.

## 1. Introduction

Copper is used as a construction metal in the central heating installations, car industry, energetics, oil refineries, sugar factories, marine environment, to name only a few of its various applications. This extensive use of copper is due to its mechanical and electric properties as well as the behaviour of its passivation layer. Acidic solutions are widely used in various industries for the cleaning of copper. The behaviour of copper in acidic media is extensively investigated, and several ideas have been presented for the dissolution process [1, 2]. To avoid the base metal attack and to ensure the removal of corrosion products/scales alone, inhibitors are extensively used. The most well-known acid inhibitors are organic compounds containing nitrogen, phosphor, sulfur, and oxygen atoms. The surfactant inhibitors have many advantages such as high inhibition efficiency (IE), low price, low toxicity, and easy production [3–5]. The interactions between the inhibitor molecules and the metal surfaces should by all means be explained and understood in detail. In examining of these interactions, theoretical approaches

applied can be very useful [6–10]. Many *N*-heterocyclic compounds have been used for the corrosion inhibition of metals, such as imidazoline [11], triazole [12–14], tetrazole [15], pyrrole [16], pyridine [17], pyrazole and bipyrazole [18, 19], pyrimidine [20], pyridazine [21], and some derivatives. Some heterocyclic compounds containing a mercapto group have been developed as copper corrosion inhibitors. These compounds include: 2-mercaptobenzothiazole [22], 2,4-dimercaptopyrimidine [23], 2-amino-5-mercaptothiadazole, 2-mercaptothiazoline [24], potassium ethyl xanthate [25–28] and indole and derivatives [29]. Among the numerous organic compounds tested and industrially applied as corrosion inhibitors, nontoxic ones are far more strategic now than in the recent past. These compounds include such amino acids [30–32] and derivatives as cysteine [33].

In the past two decades, the research in the field of *green* corrosion inhibitors has been addressed towards the goal of using cheap effective molecules at low or *zero* environmental impact. These compounds include purine and adenine, which have been tested for copper corrosion in chloride [34, 35], sulfate [36], and nitrate solutions [37].

Ionic liquids (ILs) are molten salts with melting points at/or below ambient temperature, which are composed of organic cations and various anions. Configuration of ILs consists of an amphiphilic group with a long chain, hydrophobic tail, and a hydrophilic polar head. Usually, ILs have nitrogen, sulphur, and phosphorus as the central atoms of cations, such as imidazolium, pyrrolidinium, quaternary ammonium, pyridinium, piperidinium, sulfonium and quaternary phosphonium. Currently, functionalized IL is a very noticeable topic in the field of IL research. Introducing different functional groups into cations provides a great deal of ILs with new structures that can markedly change the physicochemical properties of ILs, and it also affords more choices for applications of ILs in electrochemical devices.

Imidazolium compounds are reported to show corrosion resistant behavior on mild steel [38], copper [39, 40], and aluminium [41]. It was found that the action of such inhibitors depends on the specific interaction between the functional groups and the metal surface, due to the presence of the  $-C=N-$  group and electronegative nitrogen in the molecule. Ionic liquids and different types of surfactants base inhibitors are well known to have a high activity in acid medium [42, 43] and therefore are used in an oil field to minimize carbon-dioxide-induced corrosion [44, 45]. Among many kinds of functionalized ionic liquids ether-functionalized ILs have been investigated intensively, and ether groups have been successfully introduced in to imidazolium cations [46–52].

However, no substantial information is available on pyridinium ionic liquids being used as corrosion inhibitors of copper.

The present work describes a study of the corrosion of copper in 0.5 M  $PO_4^{3-}$  solutions of pH 2 and 4 without and with different concentrations of 1-Butyl-4-methylpyridinium tetrafluoroborate (4MBPBF<sub>4</sub>), based on copper stationary disc electrode voltammetry measurements and scanning electron microscope. Moreover, the thermodynamic functions were appointed for the adsorption process and to gain more information about the mode of adsorption of the inhibitor on the surface of copper.

## 2. Experimental Methods

**2.1. Solutions.** 1-Butyl-4-methylpyridinium tetrafluoroborate (4MBPBF<sub>4</sub>) (>99.8%) was purchased from Fluka. The molecular structures of compound are shown in Figure 1. It is worth to notice that 4MBPBF<sub>4</sub> is not flat molecule. The 4MBPBF<sub>4</sub> is stable in air, water, and in majority organic solvents. However, this compound is well enough solvable in water. All the solutions were prepared using analytical grade reagent and triple distilled water (resistivity 13 M $\Omega$  cm). The 4MBPBF<sub>4</sub> was dissolved at concentrations in the range of 1.0–50.0 mM in 0.5 M  $PO_4^{3-}$  solutions of pH 2 and 4. During the measurements, the solution was not stirred or deaerated.

**2.2. Electrodes and Apparatus.** The working electrode was a home-made stationary disk electrode (SDE) of Specpure copper (Johnson Matthey Chemicals Ltd.) with  $r = 0.240$  cm

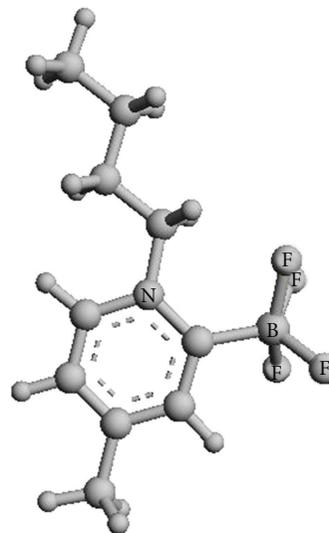


FIGURE 1: Molecular structure ionic liquid: 1-Butyl-4-methylpyridinium tetrafluoroborate (4MBPBF<sub>4</sub>).

and  $A = 0.181$  cm<sup>2</sup>. Prior to each experiment the working electrode was mechanically polished to mirror gloss by using 1000 and 2000-grade emery papers. Then the electrode was washed several times interchangeably with bidistilled water and ethanol. Finally, SDE was dried using a stream of air. Such pretreatment of the disk was repeated after each voltammetric measurement. Other details were published in [53–56]. All the surface-area-dependant values are normalized with respect to the geometric surface area of the working electrode.

Electrode potentials were measured and reported against the external saturated calomel electrode with NaCl solution (SCE(NaCl)) coupled with a fine Luggin capillary. To minimize the ohmic contribution, the capillary was kept close to the working electrode. A platinum (purity 99.99%) wire was used as an auxiliary electrode. Auxiliary electrode was individually isolated from the test solution by a glass frit.

All voltammetric experiments were performed using a Model EA9C electrochemical analyzer, controlled via Pentium computer using the software Eagrah V. 4.0.

**2.3. Scanning Electron Microscope.** A scanning electron microscope (SEM) PHILIPS XL 30 was used to study the morphology of the copper surface in the absence and presence of the inhibitor. Samples were attached on top of an aluminum stopper by means of 3 M carbon conductive adhesive tape (SPI).

**2.4. Potentiodynamic Polarization Measurements.** Electrochemical experiments were carried out in a classical three-electrode glass cell. The cell was open to air. The degreased SDE was quickly inserted into the solution and immediately cathodically polarized at  $-1100$  mV (SCE(NaCl)) for 3 min to reduce any oxide on the copper surface. The polarization curves were obtained using the linear potential sweep (LSV)

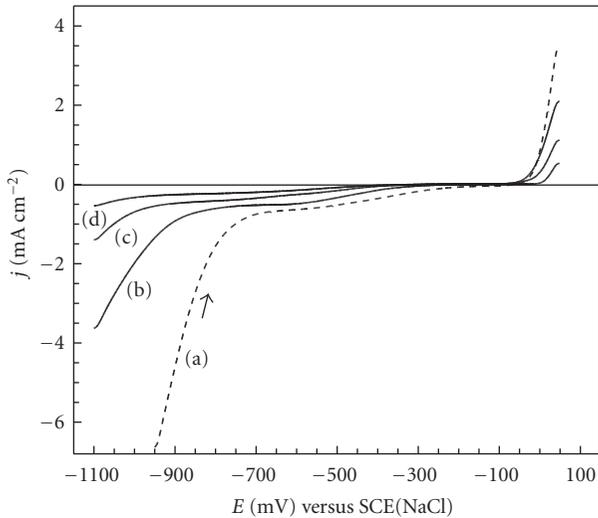


FIGURE 2: Some chosen polarization curves of the copper electrode in 0.5 M  $\text{PO}_4^{3-}$  solutions containing different concentrations of 1-Butyl-4-methylpyridinium tetrafluoroborate: (a) 0, (b) 1.0, (c) 10.0, and (d) 50.0 mM, pH 4,  $dE/dt$   $1 \text{ mV s}^{-1}$ .

technique. The scan started from the cathodic ( $-1100 \text{ mV}$ ) to the anodic direction with the scan rate of  $1 \text{ mV s}^{-1}$ . Electrochemical experiments were repeated many times, and the average values of the current were used.

All experiments were carried out using an air thermostat with the forced air circulation.

### 3. Experimental Results and Discussion

**3.1. Polarization Behaviour of Copper.** The effect of 1-Butyl-4-methylpyridinium tetrafluoroborate (4MBPBF<sub>4</sub>) on the corrosion reactions of copper was determined by polarization measurements at  $20^\circ\text{C}$ . Figure 2 shows example of polarization curves for the copper electrode in 0.5 M  $\text{PO}_4^{3-}$  solutions of pH 4 without and with different concentrations of 4MBPBF<sub>4</sub>. Similar curves were recorded for solution of pH 2. It is clear that the presence of different concentrations of the inhibitor decreases the current densities and reduces both of the cathodic and anodic current densities in comparison to those recorded in the additive-free solution. However, in case of more acid solutions (pH 2) were observed smaller changes in the cathodic and anodic current densities. The decrease in current densities could be attributed to the decrease in the phosphate ions attack on the copper surface due to the adsorption of the inhibitor molecules at the copper/solution interface.

**3.1.1. Corrosion Parameters.** The corrosion kinetic parameters were calculated on the basis of cathodic and anodic potential versus current characteristics in the Tafel potential region (Figure 3). The corrosion parameters such as corrosion potential ( $E_{\text{corr}}$ ), corrosion current density ( $j_{\text{corr}}$ ), and cathodic ( $b_c$ ) and anodic ( $b_a$ ) Tafel slope are listed in Table 1. It is worth noticing that addition of the 4MBPBF<sub>4</sub>

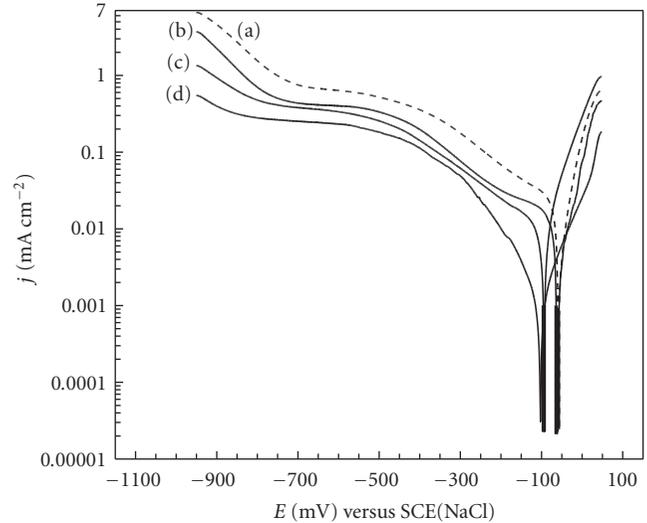


FIGURE 3: Some chosen Tafel plots of the copper electrode in 0.5 M  $\text{PO}_4^{3-}$  solutions containing different concentrations of 1-Butyl-4-methylpyridinium tetrafluoroborate: (a) 0, (b) 1.0, (c) 10.0 and (d) 50.0 mM, pH 2,  $dE/dt$   $1 \text{ mV s}^{-1}$ .

causes more negative shift in corrosion potential values independently from pH solutions. Hence small changes in potentials can be a result of the competition of the cathodic and the anodic inhibiting reactions.

The corrosion current density (Table 1) decreased when the concentrations of 1-Butyl-4-methylpyridinium tetrafluoroborate were increased for both solutions of pH 2 and 4. This indicates the inhibiting effect of 4MBPBF<sub>4</sub> on corrosion of copper. The decrease in cathodic ( $b_c$ ) and anodic ( $b_a$ ) or the increase in ( $b_a$ ) only in case of solutions of pH 4 Tafel slopes (Table 1) indicated that the 1-Butyl-4-methylpyridinium tetrafluoroborate molecules are adsorbed on both the anodic and cathodic sites resulting in an inhibition of both anodic dissolution of copper and cathodic reduction reactions. Moreover, these inhibitors cause small change in the cathodic and anodic Tafel slopes, indicating that 4MBPBF<sub>4</sub> is first adsorbed onto copper surface and therefore impedes the reaction by merely blocking the reaction sites of copper surface without affecting the cathodic and anodic reaction mechanism [57].

**3.1.2. Polarization Resistance.** The polarization resistance ( $R_p$ ) values are related to the corrosion current density ( $j_{\text{corr}}$ ), which can be calculated from the equation:

$$R_p = \left[ \frac{b_a b_c}{2.303(b_a + b_c)} \right] \times \left[ \frac{1}{j_{\text{corr}}} \right]. \quad (1)$$

The  $R_p$  values listed in Table 1 are used to estimate the corrosion inhibition effect of the inhibitor. The addition of 1-Butyl-4-methylpyridinium tetrafluoroborate to the phosphate solutions produced higher  $R_p$  values than the blank solution indicating the formation of a protective layer on the electrode surface. Hence, the polarization resistance values increase with an increase in the concentration of 4MBPBF<sub>4</sub>

TABLE 1: Corrosion parameters and polarization resistance of copper electrode in 0.5 M  $\text{PO}_4^{3-}$  solutions in the absence or presence of different concentrations of 1-Butyl-4-methylpyridinium tetrafluoroborate (4MBPBF<sub>4</sub>) of pH 2 and 4 at 20°C.

Inhibitor	pH	Concentration inhibitor (mM)	$-E_{\text{corr}}$ (mV)	$j_{\text{corr}}$ ( $\mu\text{A cm}^{-2}$ )	$-b_c$ (mV dec <sup>-1</sup> )	$b_a$ (mV dec <sup>-1</sup> )	$R_p$ ( $\Omega \text{cm}^2$ )
Blank	2	0.0	60	29.0	300	75	898
		1.0	64	16.0	280	70	1519
		5.0	79	13.2	277	67	1846
		10.0	94	10.5	275	65	2174
		25.0	99	6.5	228	63	5158
		50.0	104	2.4	180	60	8141
Blank	4	0.0	60	20.0	240	160	2084
		1.0	200	10.0	175	190	3955
		5.0	240	8.0	148	291	5987
		10.0	278	5.0	120	400	8016
		25.0	273	3.4	115	410	13478
		50.0	268	1.2	110	420	27824

for both solutions of pH 2 and 4. It seems that protective layer created on surface of copper is the most tight in of less acid solution about the largest concentration of 1-Butyl-4-methylpyridinium tetrafluoroborate.

3.1.3. *Inhibition Efficiency.* Inhibition efficiency (IE) can also be calculated from polarization tests by using the following equation [58, 59]:

$$IE(\%) = \left( \frac{j_o - j_{\text{corr}}}{j_o} \right) \times 100, \quad (2)$$

where  $j_o$  and  $j_{\text{corr}}$  are the corrosion current densities in the absence and presence of inhibitor, respectively.

The inhibition efficiency depends on both the nature and the concentration of the investigated compounds. The calculated inhibition efficiencies are presented in Figure 4. In the presence of 1-Butyl-4-methylpyridinium tetrafluoroborate solution of pH 2 and 4, the inhibition efficiency increases with an increase in the concentration of inhibitor. This confirms the inhibiting character of 1-Butyl-4-methylpyridinium tetrafluoroborate. However, IE is higher in case of solution of pH 4 than 2. It is obvious that in the presence of 1-Butyl-4-methylpyridinium tetrafluoroborate solution of pH 2 the film on copper does not cover tightly the surface and hence does not protect it prior to corrosion of Cu in an adequate degree.

3.1.4. *Corrosion Rate.* The corrosion current density ( $j_{\text{corr}}$ ) was converted into the corrosion rate ( $k_r$ ) by using the expression [60]:

$$k_r \left( \frac{\text{mm}}{\text{year}} \right) = 3.268 \times 10^{-3} \left( \frac{j_{\text{corr}} \times M_{\text{Cu}}}{n\rho} \right), \quad (3)$$

where  $M_{\text{Cu}}$  is the molecular weight of copper,  $n$  is the number of electrons transferred in the corrosion reaction, and  $\rho$  is the density of Cu ( $\text{g cm}^{-3}$ ).

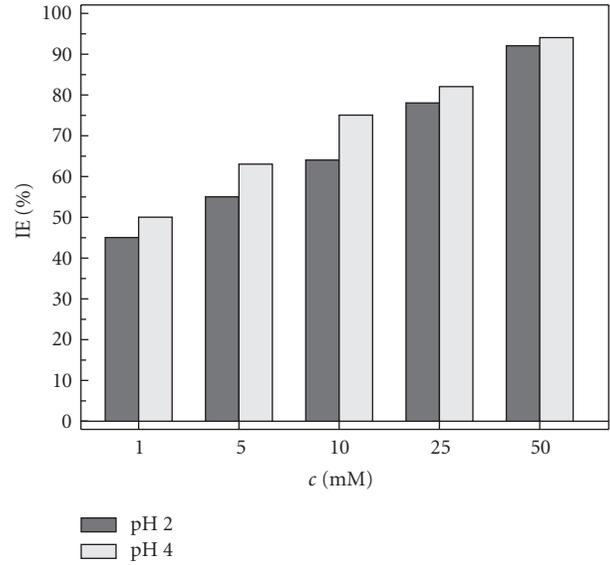


FIGURE 4: Inhibition efficiency of corrosion of copper in 0.5 M  $\text{PO}_4^{3-}$  solution with different concentrations of 1-Butyl-4-methylpyridinium tetrafluoroborate of pH 2 and 4.

The values of the copper corrosion rate in the absence and the presence of inhibitor for solution of both pH Values are presented in Table 2. The corrosion rate of copper is significantly reduced as a result of the reduction in the corrosion current densities. The protective layer on surface of metal causes that the corrosion rate to be more diminishes in case of less acid solution of phosphates.

3.2. *Scanning Electron Microscopy Studies.* The surface morphology of copper samples immersed in 0.5 M  $\text{PO}_4^{3-}$  (pH 2 and 4) for 24 hours in the absence and in the presence of 50.0 mM of 1-Butyl-4-methylpyridinium tetrafluoroborate

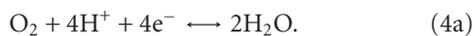
TABLE 2: Corrosion rate of copper in 0.5 M  $\text{PO}_4^{3-}$  solutions in the absence or presence of different concentrations of 1-Butyl-4-methylpyridinium tetrafluoroborate (4MBPBF<sub>4</sub>) of pH 2 and 4.

Concentration of 1-Butyl-4-methylpyridinium tetrafluoroborate (mM)	$k_r$ (mm/year)	
	pH 2	pH 4
0	0.67	0.46
1.0	0.37	0.23
5.0	0.31	0.18
10.0	0.24	0.12
25.0	0.15	0.08
50.0	0.06	0.03

was studied by scanning electron microscopy (SEM). The solutions were not degassed.

Figure 5 show the surface morphology of copper specimens (a) before and (b) after being immersed in corrosive solution (pH 2). The photograph (b) reveals that the surface was strongly damaged in absence of the inhibitor. Figures 5(c) and 5(d) show SEM images of the surface copper specimens after immersion (for the same time interval) in corrosive solution containing additionally 50.0 mM of 1-Butyl-4-methylpyridinium tetrafluoroborate of pH 2 and 4, respectively. In the presence of the inhibitor the film precipitates on the surface of copper. The SEM photographs show that protective layer does not cover tightly the surface, and, hence does not protect the Cu surface to an adequate degree especially in case of solution of pH 2. Phosphate ions, oxygen and water penetrate the protective film through pores, flaws or other weak spots what results in the further corrosion of copper. In order to check the results of action by aggressive solution, the protective layer was removed from surface of copper. The layer was well adhered to the surface of the metal, and the removal of it was really difficult. Therefore ultrasonic water bath was used. The sample was shaken in diluted acetic acid and rinsed in propanol. Figure 5 presents samples after the removal of the inhibiting film for pH 4 (Figure 5(e)) and 2 (Figure 5(f)). However, received results indicated that more tight protective layer was forming in solution of pH 4 (Figure 5(e)). Moreover, in phosphate solution the 4MBPBF<sub>4</sub> acts better as the inhibitor in less acidic environment.

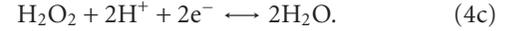
**3.3. Mechanism of Corrosion Inhibition.** Regarding the mechanism the oxygen reduction reaction on copper in acidic solutions a lot of work has been carried out [61–67]. The cathodic global reaction in an aerated aqueous phosphate solution could be described as follows:



However, the first cathodic wave is attributed to reaction:

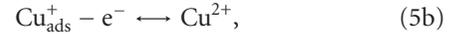


In the more negative potential at the electrode, surface occurs the next reaction:



Furthermore, reaction (4a) is strongly influenced by potential [66].

The dissolution process of copper (anodic corrosion reaction) at low overpotentials runs according to the following steps [68–70]:



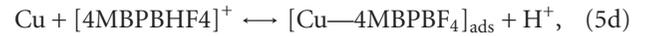
where the  $\text{Cu}_{\text{ads}}^+$  is an adsorbed monovalent species of copper at the electrode surface.

The inhibition effect of 1-Butyl-4-methylpyridinium tetrafluoroborate on the copper surface could be explained as follows

The inhibitor of 4MBPBF<sub>4</sub> can be protonated in acidic solutions:



Then the inhibitor molecules adsorb through electrostatic interactions between the negatively charged copper surface and positively charged  $[4\text{MBPBHF}_4]^+$ . However, the electrode carried the negative charge, therefore  $[4\text{MBPBHF}_4]^+$  ions should be first adsorbed directly on copper to probably form a protective layer at active sites:



and blocks the further oxidation reaction of  $\text{Cu}_{\text{ads}}^+$  to  $\text{Cu}^{2+}$  (reaction (5b)). Moreover, the inhibitor molecules lead to the blocking of the transfer of oxygen from the bulk solution to the copper/solution interface that is going to reduce the cathodic reaction of oxygen (reaction (4a)). This indicates that the presence in phosphate solution of 4MBPBF<sub>4</sub> affects both the cathodic and anodic reactions, therefore the, compound acts as a mixed-type inhibitor. The proposed mechanism of corrosion inhibition of copper by 4MBPBF<sub>4</sub> in phosphate solutions (reactions (4a)-(5a)) requires the confirmation through making additional research.

However, exhausting information regarding mechanism of corrosion inhibition can be obtained on the basis of thermodynamic measurements.

**3.4. Effect of Temperature.** The effect of temperature on the corrosion of copper in 0.5 M  $\text{PO}_4^{3-}$  solution in the absence and presence of 10.0 mM of 1-Butyl-4-methylpyridinium tetrafluoroborate of pH 2 and 4 at temperature ranging from 303 to 343 K was investigated by potentiodynamic polarization measurements. The corrosion parameters and the inhibition efficiency are presented in Table 3. The corrosion potential and cathodic and anodic Tafel slope change similarly in case of low temperature of solutions (Table 1). Therefore, the growth of temperature of solutions does not influence the change of inhibition mechanism. Worth

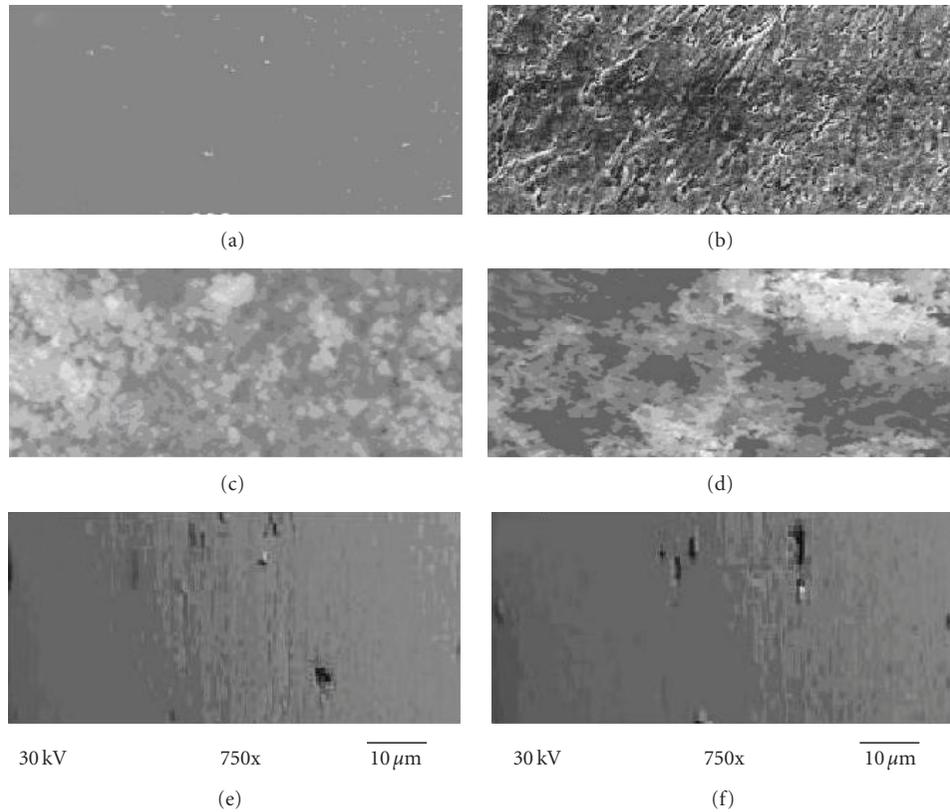


FIGURE 5: SEM micrographs of the surface of copper: (a) before, (b) after being immersed in 0.5 M  $\text{PO}_4^{3-}$  (pH 2) for 24 hours, (c), (d) corrosive solution contained additionally 50.0 mM of 1-Butyl-4-methylpyridinium tetrafluoroborate of pH 4 and 2, respectively, after removal of the inhibiting film for pH: (e) 4 and (f) 2 (magnification 750x).

noticing is that the corrosion current density increases and inhibition efficiency decreases with increasing temperature, which indicates desorption of the inhibitor molecules from the surface of copper with rising temperature of solutions.

**3.4.1. Thermodynamic Activation Parameters.** Thermodynamic activation parameters are important to study the inhibitive mechanism. The mechanism of the inhibitor action can be deduced by comparing the apparent activation energies,  $E_a$ , in the presence and absence of the corrosion inhibitor. Activation parameters such as  $E_a$ , the enthalpy of activation,  $\Delta H_a$ , and the entropy of activation,  $\Delta S_a$ , were calculated from an Arrhenius-type plot [71, 72]:

$$j_{\text{corr}} = A \exp\left(\frac{-E_a}{RT}\right), \quad (6)$$

where  $A$  is the Arrhenius constant,  $E_a$  is the apparent activation energy,  $R$  is the universal gas constant, and  $T$  is the absolute temperature. An alternative formula of the Arrhenius equation is the transition state equation [73]:

$$j_{\text{corr}} = \left(\frac{RT}{Nh}\right) \exp\left(\frac{\Delta S_a}{R}\right) \exp\left(\frac{-\Delta H_a}{RT}\right), \quad (7)$$

where  $N$  is the Avogadro's constant,  $h$  is the Planck's constant,  $\Delta S_a$  is the change of entropy for activation, and

$\Delta H_a$  is the change of enthalpy for activation. Plots of  $\ln(j_{\text{corr}})$  versus  $1/T$ , and  $\ln(j_{\text{corr}}/T)$  versus  $1/T$  give straight lines with slopes of  $-E_a/R$  and  $1/T\Delta H_a/R$ , respectively. The intercepts, which can then be calculated, will be  $[\ln(R/Nh) + (\Delta S_a/R)]$  for the Arrhenius and transition-state equations, respectively. Figures 6 and 7 represent the data plots in the absence and presence of 4MBPBF<sub>4</sub> of pH 2 and 4. The calculated thermodynamic activation parameters are listed in Table 4. The values of  $E_a$  and  $\Delta H_a$  in the presence of 10.0 mM 4MBPBF<sub>4</sub> are higher than those in black solutions, indicating that more energy barrier for the reaction in the presence of 4MBPBF<sub>4</sub> is attained, especially in case of pH 4. This shows that the energy barrier of the corrosion reaction increased in the presence of the inhibitor without changing the mechanism of dissolution of copper [74]. The entropy of activation,  $\Delta S_a$ , in the absence and presence of 4MBPBF<sub>4</sub> is large and negative (especially with pH 4), implying that the rate-determining step for the activated complex is the association rather than the dissociation step, which means that a decrease in disordering takes place by going from reactants to the activated complex [75].

**3.5. Adsorption Isotherm.** It has been assumed that inhibitor molecules establish their inhibition action via the adsorption of the inhibitor onto the metal surface. The adsorption processes of inhibitors are influenced by the chemical

TABLE 3: Corrosion parameters and inhibition efficiency of copper electrode in 0.5 M  $\text{PO}_4^{3-}$  solutions in the absence or presence of 10.0 mM of 1-Butyl-4-methylpyridinium tetrafluoroborate (4MBPBF<sub>4</sub>) of pH 2 and 4 at different temperatures.

Inhibitor	pH	Temperature (K)	$-E_{\text{corr}}$ (mV)	$j_{\text{corr}}$ ( $\mu\text{A cm}^{-2}$ )	$-b_c$ (mV dec <sup>-1</sup> )	$b_a$ (mV dec <sup>-1</sup> )	IE (%)
Blank		303	66	41.0	297	76	—
		313	79	53.5	299	76	—
		323	85	65.0	301	79	—
		333	94	77.3	306	82	—
		343	104	89.1	304	83	—
4MBPBF <sub>4</sub>	2	303	101	15.1	276	66	63.1
		313	109	22.4	279	69	58.1
		323	117	30.6	270	72	52.9
		333	124	39.9	279	74	48.4
		343	132	49.7	282	74	44.2
Blank		303	69	29.0	241	163	—
		313	78	36.3	240	163	—
		323	87	47.2	243	166	—
		333	97	57.5	246	169	—
		343	115	67.0	248	170	—
4MBPBF <sub>4</sub>	4	303	286	7.5	121	392	74.1
		313	295	11.0	123	401	69.6
		323	302	16.9	126	406	64.1
		333	311	23.6	128	408	59.0
		343	319	30.7	130	411	54.2

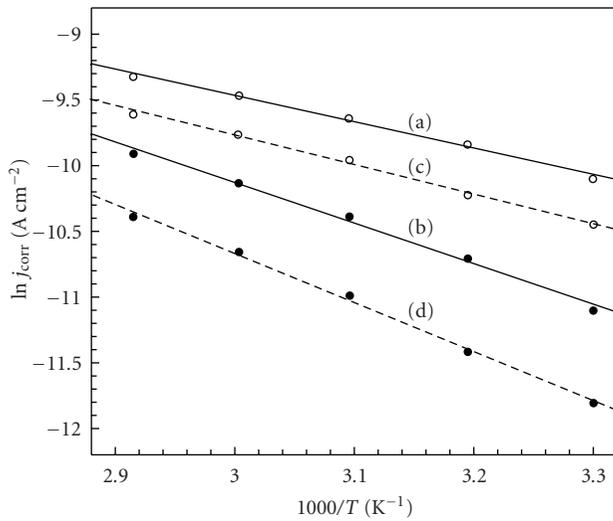


FIGURE 6: Arrhenius plots for copper in 0.5 M  $\text{PO}_4^{3-}$  solutions containing: (a), (c) 0 and (b), (d) 10.0 mM of 1-Butyl-4-methylpyridinium tetrafluoroborate. The pH of solutions was the following: (a), (b) 2 and (c), (d) 4.

structure of organic compounds, the nature and surface change of metal, the distribution of charge in molecule and the type of aggressive media [76]. The adsorption isotherm can provide the basic information on the interaction between the inhibitor and the metal surface, which depends on the degree of surface coverage,  $\Theta$  [77]. The values of

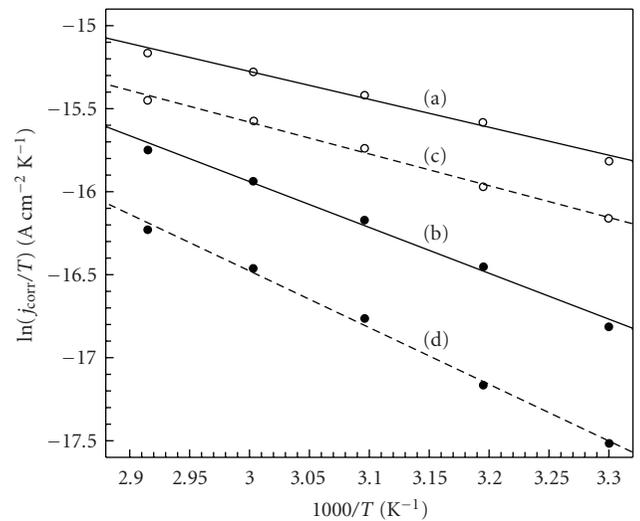


FIGURE 7: Transition state plots for copper in 0.5 M  $\text{PO}_4^{3-}$  solutions containing: (a), (c) 0 and (b), (d) 10.0 mM of 1-Butyl-4-methylpyridinium tetrafluoroborate. The pH of solutions was the following: (a), (b) 2 and (c), (d) 4.

surface coverage for different concentrations of inhibitor in 0.5 M  $\text{PO}_4^{3-}$  solutions of pH 2 and 4 were evaluated from polarization curves according equation

$$\Theta = 1 - \frac{j_{\text{corr}}}{j_0} \quad (8)$$

TABLE 4: Thermodynamic activation parameters for copper in 0.5 M  $\text{PO}_4^{3-}$  solutions in the absence or presence of 10.0 mM of 1-Butyl-4-methylpyridinium tetrafluoroborate (4MBPBF<sub>4</sub>) for pH 2 and 4.

Inhibitor	pH	$E_a$ (kJ mol <sup>-1</sup> )	$\Delta H_a$ (kJ mol <sup>-1</sup> )	$\Delta S_a$ (J mol <sup>-1</sup> K <sup>-1</sup> )
Blank	2	16.64	13.98	-282.65
4MBPBF <sub>4</sub>	2	25.66	22.98	-261.19
Blank	4	18.47	15.81	-297.69
4MBPBF <sub>4</sub>	4	31.02	28.33	-249.59

TABLE 5: Surface coverage of copper electrode in 0.5 M  $\text{PO}_4^{3-}$  solutions for different concentrations of 1-Butyl-4-methylpyridinium tetrafluoroborate (4MBPBF<sub>4</sub>) for pH 2 and 4.

pH	Concentration (mM), 1-Butyl-4-methylpyridinium tetrafluoroborate				
	1.0	5.0	10.0	25.0	50.0
2	0.45	0.55	0.64	0.78	0.92
4	0.50	0.63	0.75	0.82	0.94

TABLE 6: Slope ( $b$ ), linear correlation coefficient ( $R^2$ ), equilibrium constant ( $K$ ), and standard free energy of adsorption ( $\Delta G_{\text{ads}}^0$ ) in 0.5 M  $\text{PO}_4^{3-}$  of 1-Butyl-4-methylpyridinium tetrafluoroborate (4MBPBF<sub>4</sub>) solutions of pH 2 and 4.

pH	$b$	$R^2$	$K$ (M <sup>-1</sup> )	$\Delta G_{\text{ads}}^0$ (kJ mol <sup>-1</sup> )
2	1.00	0.9998	$2.2 \times 10^2$	-23.3
4	1.01	0.9998	$3.8 \times 10^2$	-24.7

The values of the degree of surface coverage are listed in Table 5. It can be seen that the values of  $\Theta$  increased with an increase in the concentration of 4MBPBF<sub>4</sub>. It is also worth to notice that the degree of surface coverage is higher in case of solutions of pH 4 (Table 5). Using these values of  $\Theta$ , different adsorption isotherms can be used to deal with the experimental data. The Langmuir adsorption isotherm [78, 79] was applied to investigate the adsorption of 4MBPBF<sub>4</sub> on copper surface given by the following equation:

$$\frac{c}{\Theta} = \frac{1}{K} + c, \quad (9)$$

where  $K$  is the adsorption equilibrium constant and  $c$  is the concentration of inhibitor.

Figure 8 represents the adsorption plots of 1-Butyl-4-methylpyridinium tetrafluoroborate on copper. It should be explained that other adsorption isotherms (Frumkin and Temkin) were checked. The linear correlation coefficient was used to choose the isotherm that best fits the experimental data. It should be noted that the data fits the straight line with a slope nearly equal unity with linear correlation coefficient higher than 0.999 (Table 6) indicating that these inhibitors adsorb according to the Langmuir adsorption isotherm.

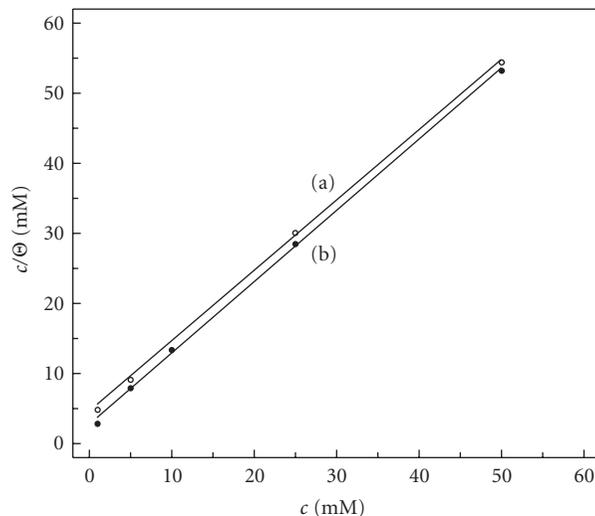
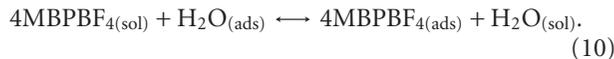


FIGURE 8: Adsorption isotherm of 1-Butyl-4-methylpyridinium tetrafluoroborate on the copper surface in 0.5 M  $\text{PO}_4^{3-}$  solutions of pH: (a) 2 and (b) 4.

The nature of corrosion inhibition has been deduced in terms of the adsorption characteristics of the inhibitor. The metal surface in aqueous solution is always covered with adsorbed water dipoles. The adsorption of inhibitor molecules from aqueous solution is a quasi-substitution process between the organic compounds in the aqueous phase and water molecules at the electrode surface [80]. The Langmuir isotherm is based on the assumption that each site of metal surface holds one adsorbed species:



In this situation, the adsorption of one molecule of 4MBPBF<sub>4</sub> is accompanied by desorption one molecule of H<sub>2</sub>O from the surface of copper. This kind of isotherm involves the assumption of no interaction between the adsorbed species on the metal surface.

A graph  $c/\Theta$  against  $c$  leads to values of  $K$ , as the equilibrium constant of the adsorption process (Figure 8). The free energies of adsorption,  $\Delta G_{\text{ads}}^0$  were calculated from the adsorption equilibrium constant using the equation [81]:

$$\Delta G_{\text{ads}}^0 = -RT \ln(55.5 \times K), \quad (11)$$

where value 55.5 is the molar concentration of water in the solution.

The adsorption equilibrium constant and the standard free energy of adsorption of 4MBPBF<sub>4</sub> for solutions of pH 2 and 4 on copper are presented in Table 6. The values of  $K$  are relatively low, meaning that interactions between 1-Butyl-4-methylpyridinium tetrafluoroborate and the metal surface are weaker. The negative values of  $\Delta G_{\text{ads}}^0$  mean that the adsorption of 4MBPBF<sub>4</sub> on copper surface is a spontaneous process, and indicates the strong interaction between the inhibitor molecules and the copper surface [82].

Generally, values of  $\Delta G_{\text{ads}}^0$  around  $-40$  kJ mol<sup>-1</sup> or lower are consistent with the electrostatic interaction between the

TABLE 7: Thermodynamic adsorption parameters for copper in 0.5 M  $\text{PO}_4^{3-}$  solutions in the presence of 10.0 mM of 1-Butyl-4-methylpyridinium tetrafluoroborate (4MBPBF<sub>4</sub>) for pH 2 and 4 at different temperatures.

pH	Temperature (K)	$K \times 10^{-2}$ ( $M^{-1}$ )	$\Delta G_{\text{ads}}^0$ ( $\text{kJ mol}^{-1}$ )	$\Delta H_{\text{ads}}^0$ ( $\text{kJ mol}^{-1}$ )	$\Delta S_{\text{ads}}^0$ ( $\text{J mol}^{-1} \text{K}^{-1}$ )
2	303	1.71	-22.69		20.14
	313	1.39	-22.17		18.40
	323	1.12	-21.65	-16.69	16.65
	333	0.93	-21.20		15.15
	343	0.79	-20.78		13.74
4	303	2.86	-23.97		15.76
	313	2.29	-23.41		13.91
	323	1.79	-22.80	-19.27	11.84
	333	1.44	-22.26		10.04
	343	1.18	-21.78		8.42

charged molecules and the charged metal surface (physisorption) [83–85]. For investigated inhibitor the values of  $\Delta G_{\text{ads}}^0$  equal  $-23.6$  and  $-24.7 \text{ kJ mol}^{-1}$  for solutions of pH 2 and 4, respectively (Table 6). The results indicate the 4MBPBF<sub>4</sub> to be physically adsorbed on the copper surface. The adsorption of the inhibitor at the metal surface is the first step in the action mechanism of inhibitors in aggressive acid media. The adsorption of 1-Butyl-4-methylpyridinium tetrafluoroborate on the copper surface makes a barrier for mass and charge transfers. This situation leads to the protection of the copper surface against the attack of aggressive solution.

**3.6. Thermodynamic Adsorption Parameters.** Thermodynamically, the free energy of adsorption,  $\Delta G_{\text{ads}}^0$ , is related to the standard enthalpy,  $\Delta H_{\text{ads}}^0$  and entropy,  $\Delta S_{\text{ads}}^0$  of the adsorption process as follows [86, 87]:

$$\Delta G_{\text{ads}}^0 = \Delta H_{\text{ads}}^0 - T\Delta S_{\text{ads}}^0 \quad (12)$$

Moreover, the standard enthalpy of adsorption could be calculated according to the Van't Hoff equation

$$\ln K = -\frac{\Delta H_{\text{ads}}^0}{RT} + \text{const.} \quad (13)$$

The adsorption equilibrium constant is related to the degree of surface coverage by:

$$K = \frac{\Theta}{c(1 - \Theta)} \quad (14)$$

It should be noted that the  $K$  decreases with increasing temperature, (Table 7). This confirms earlier made admission that the molecules of 4MBPBF<sub>4</sub> are physically adsorbed on surface of copper. However, desorption process of inhibitor enhances with raising of the temperature of the solution. The free energies of adsorption of 1-Butyl-4-methylpyridinium tetrafluoroborate were calculated at different temperatures (11) and are given in Table 7. The values of  $\Delta G_{\text{ads}}^0$  are around  $-20 \text{ kJ mol}^{-1}$  indicating that the adsorption mechanism

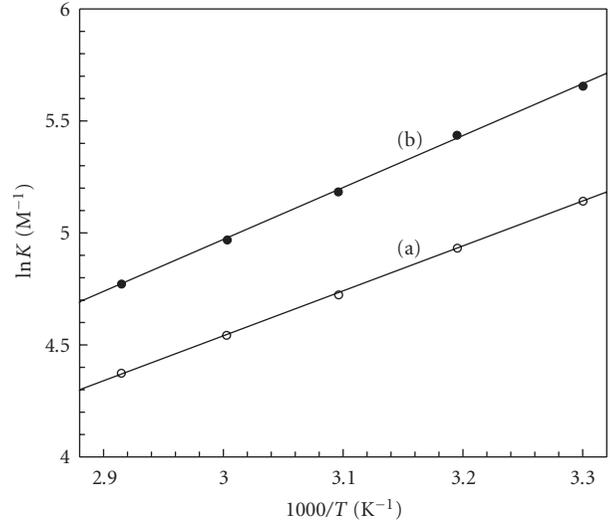


FIGURE 9: The Van't Hoff plots for the copper in 0.5 M  $\text{PO}_4^{3-}$  solutions containing 10.0 mM of 1-Butyl-4-methylpyridinium tetrafluoroborate. The pH of solutions was as the following: (a) 2 and (b) 4.

of 4MBPBF<sub>4</sub> in 0.5 M  $\text{PO}_4^{3-}$  solution of pH 2 or 4 is physisorption at the studied temperatures.

A plot  $\ln K$  versus  $1000/T$  gives of straight lines, as shown in Figure 9. The slope of the straight line is  $-\Delta H_{\text{ads}}^0/R$ . The values of the standard enthalpy are given also in Table 7. The  $\Delta H_{\text{ads}}^0$  values are negative, for that reason adsorption of 1-Butyl-4-methylpyridinium tetrafluoroborate molecules onto the Cu surface is an exothermic process. Moreover, the values of  $\Delta H_{\text{ads}}^0$  are less than  $-40 \text{ kJ mol}^{-1}$  [88], therefore, once again implying that in investigated solutions, physical adsorption is taking place.

The standard entropy of inhibitor adsorption,  $\Delta S_{\text{ads}}^0$  can be calculated from (12). The values of  $\Delta S_{\text{ads}}^0$ , are recorded in Table 7. The positive values of  $\Delta S_{\text{ads}}^0$  mean that the increase in disordering takes place by going from reactants to the Cu/solution interface, which is the driving force for the adsorption of 1-Butyl-4-methylpyridinium tetrafluoroborate onto the copper surface [89].

## 4. Conclusion

The following results can be drawn from this study.

- (1) The investigated 1-Butyl-4-methylpyridinium tetrafluoroborate (4MBPBF<sub>4</sub>) exhibits inhibiting properties for the corrosion of copper in 0.5 M  $\text{PO}_4^{3-}$  solutions of pH 2 and 4.
- (2) The inhibition efficiency (IE(%)) increased with the increase in inhibitor concentration but decreases with increasing temperature. IE at all concentrations of 4MBPBF<sub>4</sub> followed the order of pH: 4 > 2.
- (3) The of 1-Butyl-4-methylpyridinium tetrafluoroborate acts as a mixed-type inhibitor, independently from pH solutions.

- (4) The corrosion inhibition action of 1-Butyl-4-methylpyridinium tetrafluoroborate is mainly due to adsorption of 4MBPBF<sub>4</sub> on the surface of copper.
- (5) The adsorption of the investigated compound obeys the Langmuir adsorption isotherm.
- (6) The thermodynamic functions of corrosion indicate that of 1-Butyl-4-methylpyridinium tetrafluoroborate adsorbs on the copper surface by a physisorption-based mechanism involving a spontaneous and exothermic process.

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